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16. ABSTRACT

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Determination of Trace Anions in Water by Multidimensional Ion Chromatography

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Selenate, selenite, and arsenate ions were separated from the major anions chloride, nitrate, and sulfate in drinking water, surface water, and groundwater sources by collecting a selected portion of the ion chromatogram, after suppression, on a concentrator column and reinjecting at the original chromatographic conditions. Statistical detection limits varied from 0.02 to 1.2 μg of trace element depending on the minor components to be separated and on the water matrix but independent of initial sample size from 2 to 10 mL. The maximum reliably separated molar ratio was 1300 for sulfate/selenate in well water. Carbonate–bicarbonate eluent compositions were optimized for each trace ion.

Determination of trace components in the presence of major interferences is a common and troublesome problem in many areas of analytical chemistry. Several workers have reported the use of ion chromatography (IC) for the determination of trace anions individually or as peaks well-separated from other components, but no attempts to separate overlapping peaks have been reported. Wetzel et al. (*1*) showed that part-per-billion levels of individual ions in water could be determined by IC in which the traces were collected on concentrator columns, which were 50-mm lengths containing the same ion exchange resin as the separator column. Bynum et al. (*2*) reported that the IC response to 100 ppm of sulfate was reduced by the presence of more than 0.4% chloride, although the peaks were well separated. Smee et al. (*3*) used IC for the determination of fluoride, chloride, nitrate, and sulfate in natural waters. In controlled studies they found that fractional part-per-million levels of F^-, Cl^-, or NO_3^- gave about 10% greater response when the remaining three ions were added at 20- to 200-fold greater concentrations. Sulfate did not seem to be affected. The authors did not report whether chromatographic peaks overlapped.

This paper is concerned with the extraction of a component that may be completely buried under the peak of a major ion. The approach we used is the elementary one of collecting the portion of the chromatogram suspected to contain the trace ion on a concentrator column and reinjecting at the original chromatographic conditions. The term "recycle chromatography" was introduced by Porath and Bennich (*4*) for the continuous recycling of eluent in gel chromatography but is used here for the discrete operation that has also been termed "heart-cutting" (*5*, *6*). The procedure, in which no attempt is made to improve resolution through changes of the fixed or mobile phases, obviously is a special case of multidimensional chromatography or column switching (*7*).

We have chosen to illustrate the technique by the speciation of arsenic and selenium in drinking water and water supplies. The National Interim Primary Drinking Water Regulations (*8*) mandate maximum *total* concentrations of arsenic and selenium of 50 and 10 ppb, respectively, whereas nitrate nitrogen may be present at 10 ppm. Chloride and sulfate are not controlled but are typically present at several parts per million. IC can readily determine arsenate, selenite, and selenate species in water in the absence of interferences (*9*). At the permissible concentrations, however, they will usually be completely obscured by the major anions. Arsenic and selenium are ordinarily at their highest oxidation state in surface waters but that is not necessarily the case in groundwaters. When concentrations are great enough to require removal, it is important to know which species are present in designing the treatment technology. The water matrices used in this study—treated municipal drinking water, river water, and water from a shallow well—did not contain detectable amounts of the toxic anions and all experiments were made with known additions.

Although the concept of recycling to separate trace components from major interferences is simple, several limitations and conditions are immediately apparent in IC:

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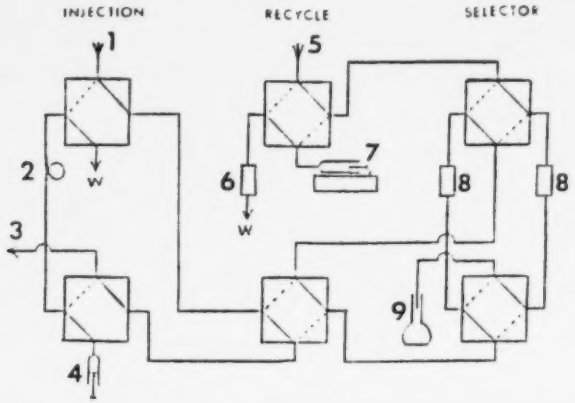

Figure 1. Valving: (1) eluent supply; (2) sample loop; (3) to separator; (4) injection port; (5) from detector; (6) dummy concentrator column; (7) syringe pump; (8) concentrator columns; (9) volumetric flask, 2, 5, or 10 mL.

1. Some form of concentration before reinjection is needed. Band spreading produces peaks eluting in a volume of several milliliters from a sample injected as 0.1 mL. The concentrator column is a convenient and effective means both for collecting and for concentrating the component.

2. Eluent suppression is necessary to retain the analyte on the concentrator.

3. The technique is not applicable to anions of weak electrolytes that are not retained by the concentrator, e.g. fluoride, cyanide, or arsenite.

4. Placing a concentrator column on line after the suppressor and detector increases the flow resistance through the system, probably requiring lower flow rates and certainly increasing back pressure on the suppressor to the extent that the fiber suppressor (*10*) cannot be used.

EXPERIMENTAL SECTION

Apparatus. A Dionex Model 10 ion chromatograph was equipped with a AG-1 guard column, AS-3 "fast run" separator column, and ASC-1 suppressor. AG-3 concentrator columns were used for introduction of the sample and for collection of and recycling of selected portions of the chromatogram. Early trials with the older AG-1 concentrators indicated that they apparently did not release the sample charge fast enough for effective focusing by the more efficient separator. Satisfactory resolution of test mixtures could only be obtained by using the same type of resin in both concentrator and separator. For recycle chromatography, the plumbing was modified as shown in Figure 1. The original injection valve was connected to two additional dual four-port slider valves. Solid lines in the figure correspond to the "Down" position of the toggle switches. The dummy concentrator in the waste line of the recycle valve was added to maintain approximately constant back pressure on the conductivity detector because the base line conductance of the suppressed eluent is highly pressure sensitive.

Concentrator columns were loaded in place with a Harvard Apparatus infusion pump at 1.5 mL min^{-1}, using a Hamilton 5-mL glass syringe with a gastight Teflon tipped plunger and Luer fitting to 0.5 mm i.d. Teflon tubing. The volume of solution loaded was measured by collecting the effluent in a volumetric flask, shown in Figure 1. All recycle runs were made at 15% pump rate (1.51 mL min^{-1}) and at room temperature (25 ± 1 °C).

Materials. Three sources of water were used as test matrices: local municipal drinking water taken from the tap; water from a shallow, unused well in a nearby community; and water from a local river drawn about 2 miles downstream from the discharge of a municipal waste treatment plant. Each sample (2–3 L) was filtered through 0.2-μm pore size membrane filter (Metricel GA-8) and stored at room temperature in flexible polyethylene bags. The major ions were determined by IC using the method of standard additions, with the results shown in Table I. The relative uncertainty of these values is about ±15%, as determined by the (negative) intercepts of the 95% confidence limits of the least-squares fit of four of five additions to the river water.

Table I. Major Ions in Water Matrices

water	ions, mg L^{-1}			
	F^-	Cl^-	NO_3^-	SO_4^{2-}
drinking	0.81	3.4	1.8	7.8
well	0.01	6.8	0.26	6.4
river	0.31	3.8	3.0	3.2

Table II. Calculated Elution Times of Nitrate and Sulfate in Various Carbonate-Bicarbonate Eluents

SO_4^{2-}, RT, min	NO_3^-, RT, min	CO_3^{2-}, mM	HCO_3^-, mM	pH
15	13.61	2.9	2.11	10.47
	13.62	3.0	1.17	10.74
	13.62	3.1	0.23	11.46
20	15.7	1.8	5.9	9.81
	15.7	2.0	3.7	10.06
	15.7	2.2	1.55	10.48
25	17.57	1.5	4.56	9.85
	17.57	1.6	3.35	10.01
	17.59	1.7	2.11	10.24

Stock solutions of 1000 ppm of the test ions were prepared from reagent grade sodium salts in water that had been purified by reverse osmosis and mixed-bed ion exchange. The stock solutions were adjusted to the composition of the Dionex standard eluent (3.0 mM $NaHCO_3$, 2.4 mM Na_2CO_3) and membrane-filtered through 0.45-μm pore size Metricel GA-6. Solutions of 1 or 10 ppm were prepared by dilution of the stock with the water under test and further dilutions were made from these shortly before injection. The municipal drinking water had to be boiled briefly to remove available chlorine before stable dilute solutions of selenite in it could be obtained.

Eluent Selection. In general, eluent compositions had to be derived for optimum resolution of each test ion. Selenate elutes later than sulfate in the standard eluent (3.0 mM $NaHCO_3$, 2.4 mM Na_2CO_3) (*9*) and was the least stringent separation. The standard eluent was used although an eluent of greater total alkalinity probably would reduce running time without a serious loss of sensitivity.

By trial it was found that selenite eluted between chloride and nitrate in an eluent that was 3.0 mM in $NaHCO_3$ and 2.0 mM in Na_2CO_3.

Arsenate can be made to elute later than sulfate in the strongly alkaline eluent proposed by Hansen et al. (*11*). Using this eluent (3.5 mM Na_2CO_3, 2.6 mM NaOH), we found a 3σ detection limit (*12*) of 0.12 μg of As(V) added to drinking water. The detection limit variance is based on deviations from the calibration line, derived both from 0.1-mL loop injections and collection of 5-mL samples in concentrator columns. We sought to improve the analytical sensitivity by shifting the elution of As to a shorter retention time, where the peak conductance would be greater, and using recycling to overcome interference by major ions. The difference in charge type of nitrate and sulfate provides an opportunity to shift their relative retention times by changing the proportions of carbonate and bicarbonate in the eluent (*13, 14*). Retention data for nitrate and sulfate in four eluent compositions were used to estimate the selectivity coefficients in eq 15 and 16 of ref 14, using carbonate and bicarbonate as the only effective eluent ions.

These empirical coefficients were then used to calculate expected retention times in 31 combinations of carbonate and bicarbonate. The results, summarized in Table II, lead to two observations: (1) decreasing total alkalinity increases both the absolute and relative retention times of nitrate and sulfate; and (2) for any choice of retention times of nitrate and sulfate, there is at least 0.5 pH unit range of eluents available for adjustment of arsenate retention. After a few additional trials an eluent composition of 3.0 mM $NaHCO_3$ and 1.5 mM Na_2CO_3 was found to elute arsenate about midway between nitrate and sulfate.

Table III. Calibration Data for Recycle Determination of Trace Anions in Water

water	intercept, S cm^{-1}	slope, S cm^{-1} g^{-1}	detection limit, μg	N
	Selenate (3.0 mM $NaHCO_3$, 2.4 mM Na_2CO_3, pH 9.72)			
drinking (1)	0.26 ± 0.15[a]	3.49 ± 0.30[a]	0.21	6
(2)	0.20 ± 0.06	2.37 ± 0.26	0.18	10
well	0.011 ± 0.03	1.166 ± 0.016	0.020	8
river	0.012 ± 0.004	1.226 ± 0.016	0.018	6
	Selenite (3.0 mM $NaHCO_3$, 2.0 mM Na_2CO_3, pH 9.24)			
drinking	−0.034 ± 0.052	2.23 ± 0.10	0.20	19
well	−0.089 ± 0.056	2.33 ± 0.16	0.18	11
river	0.77 ± 0.25	1.63 ± 0.25	1.2	13
	Arsenate (2.5 mM $NaHCO_3$, 1.5 mM Na_2CO_3, pH 9.56)			
drinking	0.024 ± 0.10	0.83 ± 0.20	0.47	6
well	−0.017 ± 0.10	0.781 ± 0.038	0.68	8
river	−0.03 ± 0.09	0.902 ± 0.045	0.83	12

[a] ± standard deviations.

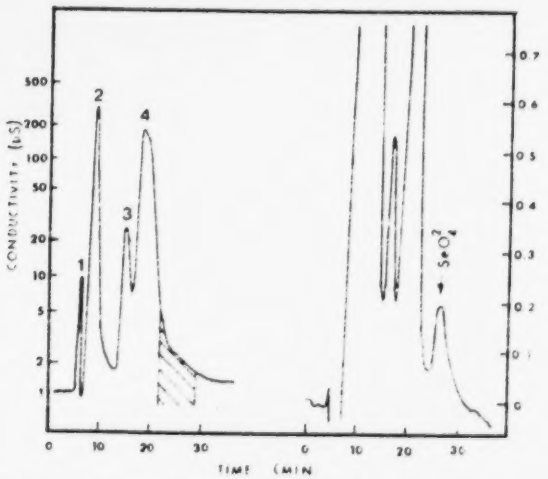

Figure 2. Selenate in drinking water: sample size, 5 mL; 10 ng of Se(VI) added; major peaks, (1) fluoride, (2) chloride, (3) nitrate, (4) sulfate. Shaded area was collected for recycle.

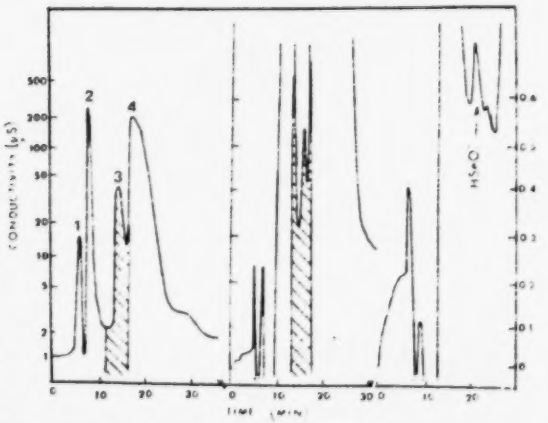

Figure 3. Selenite in drinking water, recycled twice: sample size: 10 mL, 100 ng of Se(IV) added; major peaks, (1) fluoride, (2) chloride, (3) nitrate, (4) sulfate. Shaded areas were collected for recycle.

About 3 months later arsenate was found to elute closer to sulfate, possibly because of gradual deterioration of the separator column. Increasing the bicarbonate concentration in the eluent to 2.5 mM restored the original resolution by increasing total alkalinity and reducing pH.

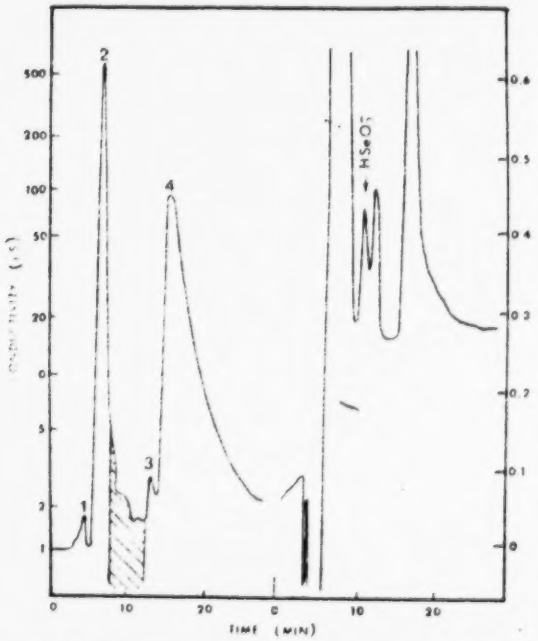

Figure 4. Selenite in well water: sample size, 5 mL; 150 ng of Se(IV) added; major peaks, (1) fluoride, (2) chloride, (3) nitrate, (4) sulfate. Shaded area was collected for recycle.

Washing. Suppressed eluent retained in the concentrator columns produced a large carbonate peak on direct reinjection. This peak obscured or interfered with everything eluting before nitrate. In the determinations of selenite, the concentrator was washed with deionized water for 5 min after collection and before injection. The wash step was omitted in the determinations of arsenate and selenate, where the carbonate did not interfere.

RESULTS AND DISCUSSIONS

Figures 2 to 5 show representative chromatograms for each of the trace anions at close to the statistical detection limit. The initial injection is shown on a logarithmic scale of conductance to include complete peaks of the major constituents. The recycle portion of the chromatogram was obtained at the linear scale, usually 1 μs cm^{-1} full-scale sensitivity. Figure 5 shows a second collection and recycling of selenite. The process can be repeated indefinitely but there is evidence (below) of [illegible] material each time.

Calibration curves for each trace ion in each matrix are summarized in Table III. Amounts of trace anion injected

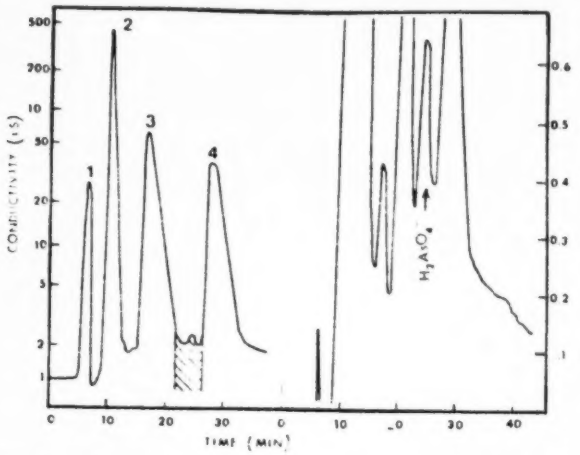

Figure 5. Arsenate in river water: sample size, 5 mL, 50 ng of As(V) added; major peaks, (1) fluoride, (2) chloride, (3) nitrate, (4) sulfate. Shaded area was collected for recycle.

were run in a randomized order and most calibrations included both 2-mL and 5-mL initial injections. Increasing the sample size allows lower concentrations of the minor constituent to be collected but does not affect the relative proportions that must be separated. Our statistical studies of mass detection limits have not revealed any significant effect of sample size among 0.1, 2.0, and 5.0 mL.

The detection limits shown in Table III are all 3σ limits (*12*), based on the standard deviation of the ordinates from the least-squares linear fit. In all cases this limit is appreciably greater than the detectability of trace amounts in individual runs, as shown in Figures 2–5. Table III reveals some disturbing features about the speciation of selenium for which we have no explanation. Selenite, in river water, showed a significant positive intercept and lower slope of the calibration curve than in the other two water matrices. On the other hand, selenate was exceptional in drinking water, having positive intercept and greater slope of the calibration curve. The first line of Table III summarizes the initial series of this study, completed in January 1983. After we found much greater precision in the determination of selenate in well and river waters, we thought the improvement might have resulted from better techniques. Therefore, the drinking water series was repeated at the end of the study (June 1983). The precision was essentially the same as in the first series, by the F test, but the slopes of the two calibration curves were different from each other and from the curves for river and well waters.

One effect of the matrix water on trace determination is the concentration of major ion interference. In the case of selenite, the major interferent is nitrate and the exceptional results in river water may be related to the high nitrate level in that medium (Table I). If that were the controlling factor, however, one would expect a greater difference between well and drinking water than was observed. Similarly, for selenate the critical separation is from sulfate, which is greatest in drinking water, but river and well water differ more in sulfate content than well and drinking water, in contrast to the calibration curves.

Because run-to-run variability limited application of the recycle technique in this study, an effort was made to identify better the sources and effects of the variance. The largest data set for this purpose consisted of determinations of selenite added to well and drinking water (30 points). Data were available for 2-, 5-, and 10-mL sample sizes in each medium. An analysis of covariance indicated that the subsets for 10-mL samples of drinking water and 5-mL samples of well water

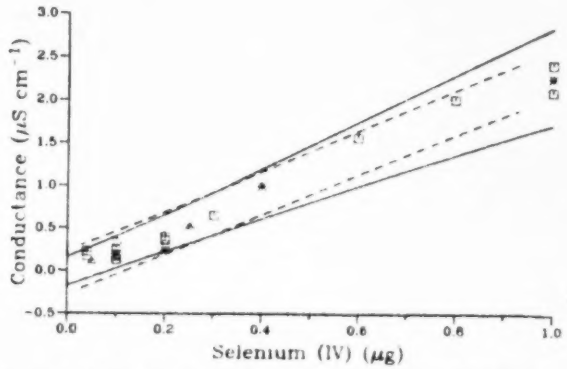

Figure 6. Calibration for selenite additions to water: □, drinking water, 2-mL samples; △, drinking water, 5-mL samples; *, well water, 2-mL samples; ○, well water, 10-mL samples. Confidence limits (95%) for a single future measurement are as follows: solid line, variance weighted; dashed lines, unweighted.

were not consistent with the remaining data, having significantly different slopes at constant intercept and different intercepts at constant slope. The five data points for 10-mL drinking water samples were all recycled twice, as shown in Figure 3, and the lower slope for that subcalibration, 2.09 μS cm^{-1} μg^{-1}, relative to 2.33 for the remainder, probably reflects a loss of material in the additional cutting and collection. The anomalous well water set consisted of only four points representing a very narrow range (0.05–0.25 μg of Se(IV)). These points had a mutual slope of only 1.02 ± 0.06 μS cm^{-1} μg^{-1} for no recognizable reason. The remaining 21 points are plotted in Figure 6.

Recently Oppenheimer et al. (*15*) have shown that detection limits calculated from calibration curves may be reduced by allowing for inhomogeneous variances, if the variance increases regularly with the concentration or amount of the calibrant. The clusters of points at 1.0, 0.2, 0.1, and 0.04 μg of Se in Figure 6 provide variance estimates that are consistent with a direct linear relation between variance and amount, although they are not sufficient to establish the pattern. We used the empirical power function to obtain a finite estimate for the blank

$$s^2 = A(1 + X)^B \quad (1)$$

Each point was weighted inversely proportional to the calculated variance estimate to obtain the weighted confidence limits shown in Figure 6. It should be noted that the weighted and unweighted 95% confidence limits in the figure are for a *single future* observation (*15*, *16*) and are not the limits of the calibration data.

The indication of nonhomogeneous variance suggested that the data also should be fitted by a robust regression analysis (*17*) using the biweight of Tukey

$$W_i = [1 - (r_i/9S)^2]^2 \quad (2)$$

where W_i is the weight of the ith point having a residual r_i from the previous regression iteration and S is the median of the absolute values of all residuals. Iteration was continued until the residuals changed less than 2×10^{-4}. The resulting linear fit had a slope of 2.322 ± 0.086 and intercept of −0.006 ± 0.039. These parameters are not significantly different from those for the conventional least-squares (unweighted) fit: slope 2.330 ± 0.077 and intercept −0.021 ± 0.036, where standard deviations of the parameters are included.

From the protolysis constants given by Baes and Mesmer (*18*) and at the pH values of the eluents, we calculated that selenate, selenite, and arsenate should each be predominantly in the doubly charged form. Biselenite (15%) is the only other ionic species amounting to more than 1% of the equilibrium

mixture. Nevertheless, the retention times for Se(IV) and As(V) are more typical of singly charged ions.

The quantitative separations that can be achieved by selective recycling will depend principally on the molar ratios of major to minor components as well as the difference in retention times. By use of the statistical detection limits of Table III and the amount of major ion in a 5-mL sample of the various waters of Table I, the greatest mole ratios separated were 1300 for sulfate/selenate in well water, 480 for chloride/selenite in well water, 60 for nitrate/selenite in drinking water, 60 for sulfate/arsenate in drinking water, and 20 for nitrate/arsenate in river water. Qualitatively, considerably better separations may be achievable, as shown by the chromatograms presented here. The critical factor appears to be how successfully the concentration of the major component is reduced in the collection step. In some cases there was no indication of the trace component in the original chromatogram.

Registry No. Arsenate, 15584-04-0; selenate, 14124-68-6; selenite, 14124-67-5; water, 7732-18-5.

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